

## (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
22 February 2001 (22.02.2001)

PCT

(10) International Publication Number  
**WO 01/12320 A1**

(51) International Patent Classification?: **B01J 23/56,**  
**B01D 53/94, B01J 35/04**

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(21) International Application Number: **PCT/GB00/03064**

(22) International Filing Date: 14 August 2000 (14.08.2000)

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(25) Filing Language: English

(81) Designated States (national): **CA, JP, MX, US.**

(26) Publication Language: English

(30) Priority Data:  
9919013.4 13 August 1999 (13.08.1999) **GB**

(84) Designated States (regional): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE).

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**Published:**

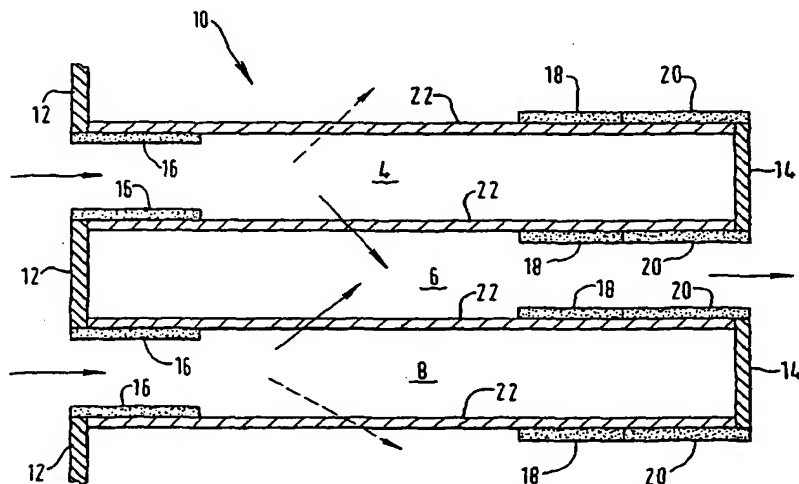
- With international search report.
- Before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments.

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For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: **CATALYTIC WALL-FLOW FILTER**



(57) Abstract: A wall-flow filter (10) for an exhaust system of a combustion engine comprises: a plurality of channels (4, 6, 8) in honeycomb arrangement, wherein at least some of the channels (6) are plugged (12) at an upstream end and at least some of the channels (4, 8) not plugged at the upstream end are plugged (14) at a downstream end; an oxidation catalyst (16) on a substantially gas impermeable zone at an upstream end of the channels (4, 8) plugged at the downstream end; and a gas permeable filter zone (22) downstream of the oxidation catalyst for trapping soot, characterised in that in an exhaust system, preferably a diesel exhaust system, the oxidation catalyst, which preferably includes a platinum group metal, is capable of generating sufficient NO<sub>2</sub> from NO to combust the trapped soot continuously at a temperature less than 400 °C.

**CATALYTIC WALL-FLOW FILTER**

This invention relates to a wall-flow filter, and in particular to a wall-flow filter  
5 including a catalyst.

Exhaust gases of a combustion engine contain a number of components linked  
with damaging health and the environment. One of these is the soot component. A way  
of controlling the amount of soot in the exhaust gas is to use a filter downstream from the  
10 exhaust manifold, the idea being to burn (oxidise) soot trapped on the filter, thereby  
regenerating the filter.

A known type of soot filter is the wall-flow filter. This filter can be made, for  
example, from a ceramic monolith including channels in a honeycomb arrangement. A  
15 typical embodiment has each channel plugged at one or other end thereof, and at the  
opposite end to the laterally and vertically adjacent channels. When viewed from either  
end, the alternately plugged and open ends of the channels take on the appearance of a  
chessboard. The ceramic material from which the filter can be made has a pore size  
sufficient to allow gas permeability so that the pressure drop across the filter is relatively  
20 low, but which prevents the passage of soot. Thus soot is filtered from the exhaust gases.

EP-A-0341832 and corresponding case US-A-4,902,487 describes a process and  
treatment system for soot-containing exhaust gas, the gas also containing nitric oxide  
(NO), which process comprising passing the gas unfiltered over an oxidation catalyst to  
25 convert NO to nitrogen dioxide (NO<sub>2</sub>), collecting the soot on a downstream filter and  
combusting the collected soot continuously at under 400°C by reaction with the NO<sub>2</sub>; and  
there have been recent proposals to add further steps to that process and system, for  
example nitrogen oxides (NO<sub>x</sub>) removal steps (see EP-A-0758713). EP-A-0341832 and  
US-A-4,902,487 describe Johnson Matthey's Continuously Regenerating Trap (CRT™)  
30 technology and are incorporated herein by reference.

In the process described in EP-A-0341832 the oxidation step and the filter  
combustion step are carried out in two different honeycombs each in a separate shell or  
can or mounted within a single can. However, there are problems in adopting either

embodiment. A problem with the former embodiment is that there can be limited space under-floor on a vehicle to mount each can. In the latter embodiment, a problem is that the construction of the can is complicated. If further downstream process steps are required these problems are exacerbated.

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We have now found that these and other problems can be overcome or reduced by carrying out each of the treatment steps on a single wall-flow filter or single "brick". US-A-5,089,237 discloses a soot burn-off filter for an exhaust system of a combustion engine, which filter includes a porous ceramic honeycomb block having channels plugged alternately at the ends to define a flow path through the partition walls of the channels, the walls at the inlet end having a catalytic coating. We understand from this document that the filter is used in a discontinuous process in which soot is allowed to accumulate on the filter and is periodically burnt off by raising the temperature and ensuring that sufficient oxygen ( $O_2$ ) is available. Owing to the combustion of a substantial quantity of soot in a relatively small space, temperatures high enough to produce destructive effects on the filter are readily attained. To limit such effect the filter of US-A-5,089,237 provides a gas-tight region in the partition walls at the downstream end of the upstream channels. Although the catalytic coating is stated to lower the temperature at which soot combustion takes place, it evidently does not make the gas-tight region unnecessary.

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According to one aspect, the invention provides a wall-flow filter for an exhaust system of a combustion engine, which filter comprises: a plurality of channels in honeycomb arrangement, wherein at least some of the channels are plugged at an upstream end and at least some of the channels not plugged at the upstream end are plugged at a downstream end; an oxidation catalyst on a substantially gas impermeable zone at an upstream end of the channels plugged at the downstream end; and a gas permeable filter zone downstream of the oxidation catalyst for trapping soot, characterised in that in an exhaust system the oxidation catalyst is capable of generating sufficient  $NO_2$  from  $NO$  to combust the trapped soot continuously at a temperature less than  $400^\circ C$ .

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The term "continuously" means that collected soot is combusted in a continuous

exhaust gas flow; it thus excludes (except in the event of malfunction) the combustion of a large amount of accumulated soot. It does, however, encompass relatively minor variations in the level of collected soot and in the gas composition in response to normal variations of engine operating conditions and to short-term injection of reductant or NOx specific reactants in order to remove NOx downstream of the filter.

For the avoidance of doubt, by "absorb" herein, we mean to hold a relevant species on a relevant surface of a body (otherwise "adsorb") and/or to hold a species below the surface of a body i.e. within the body.

Exhaust gases from a combustion engine also contain unburnt hydrocarbon (HC), carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), steam (H<sub>2</sub>O(g)) and nitrogen (N<sub>2</sub>). Its content of NOx comprises NO and NO<sub>2</sub>, the majority being NO. At least sufficient NOx should be present to provide, after the catalytic oxidation of NO to NO<sub>2</sub>, at least enough NO<sub>2</sub> to oxidise the collected soot as it is formed, or after a small accumulation of soot. As described in the above mentioned EP-A-0341832, and in PCT application no. GB00/02062, additional NOx may be supplied by e.g. injecting nitric acid or the product of local oxidation of ammonia (NH<sub>3</sub>) or an ammonia precursor, such as urea.

The filter of the present invention provides a gaseous flow path defined in part by the open ends of each channel plugged at the downstream end, and the pores of the gas permeable wall of the channel. Soot in the gaseous exhaust enters the channel, but cannot pass through the pores of the channel wall. Thus soot is filtered from the gaseous exhaust by the pores of the filter. Furthermore, the gaseous exhaust is forced to flow over the entire zone supporting the oxidation catalyst, as the wall of the filter on which it is supported is substantially gas impermeable. This achieves the best possible yield of NO<sub>2</sub> from NO at a given temperature and also avoids caking the catalyst in soot.

Preferably, the arrangement of channels plugged at the upstream and downstream ends of the filter is such that each channel of the filter is plugged at one or other end thereof, and at the opposite end to the laterally and vertically adjacent channels, although other configurations can be used. For example, in an arrangement of striated appearance, a first longitudinal array of channels is plugged at one end, and the longitudinal arrays of

channels either side of the first array are plugged at the opposite ends of the filter, and so on. The provision of a filter including at least some unplugged channels, thereby to act as a by-pass to the filter channels, is also within the ambit of the present invention. The unplugged channels can also be used to introduce a reactant required downstream of the wall-flow filter zone.

The channels are preferably square in cross-section but can be any other shape such as circular, rectangular, hexagonal or triangular.

Preferably, the oxidation catalyst, which is advantageously a compound including a platinum group metal (PGM), such as platinum (Pt) or palladium (Pd), blocks the filter pores in the gas impermeable zone, thereby making the zone substantially gas impermeable. Filter-grade materials for making the filter suitably have a mean pore diameter in the range  $0.4$  to  $20 \times 10^{-3}$  inch ( $1$  to  $50 \mu\text{m}$ ) for gas treatments at about atmospheric pressure, but other values may be more appropriate for liquids or at higher or lower pressures. Although it is possible to manufacture a filter in which the filter material itself is gas impermeable or the pore size is graded so that the upstream part of channels plugged at the downstream end are gas impermeable but gas permeability increases towards the filter zone, we prefer that the filter material is of uniform pore size and that zones supporting the catalyst are rendered gas-impermeable by applying materials to them. When the filter is ceramic, it may be the product of shaping (e.g. by extrusion) and a composition containing sufficient fugitive material to leave, once removed e.g. by calcination, the required pores. The filter, whether ceramic or metal, may be the product of moulding and sintering a powder, possibly via foam. Whilst the filter material can be metal, we prefer it to be made of a ceramic material such as cordierite, alumina, mullite, silicon carbide, zirconia or sodium/zirconia/phosphate. The honeycomb has typically at least 50 cells per square inch ((cpsi)(  $7.75 \text{ cm}^{-2}$ ), possibly more, e.g. up to 800 cpsi ( $124 \text{ cm}^{-2}$ ). Generally the range 100-600 cpsi ( $15.5$ - $93 \text{ cm}^{-2}$ ) is preferred, of which 200-400 cpsi ( $31$ - $62 \text{ cm}^{-2}$ ) is most preferred.

According to preferred embodiments, the downstream channels of the filter include a catalyst for a NOx absorber (or NOx trap) and optionally a NOx reduction catalyst or Selective Catalytic Reduction (SCR) catalyst downstream of the NOx

catalyst or Selective Catalytic Reduction (SCR) catalyst downstream of the NO<sub>x</sub> absorber. The combination of CRT<sup>TM</sup> technology and the SCR of NO<sub>x</sub> with a nitrogen-containing compound, such as NH<sub>3</sub> or urea, is described in our WO 99/39809. In a further embodiment, the channels upstream of the oxidation catalyst can include a sulphur oxides (SO<sub>x</sub>) absorber (SO<sub>x</sub> trap). The upstream SO<sub>x</sub> absorber can be included in embodiments with or without the NO<sub>x</sub> absorber or NO<sub>x</sub> reduction catalyst or SCR catalyst. As with the zone including the oxidation catalyst, in embodiments including one or more of the SO<sub>x</sub> absorber, NO<sub>x</sub> absorber or NO<sub>x</sub> reduction catalyst or SCR catalyst, the zones of each catalyst or absorber is substantially gas impermeable, and the gas impermeability is preferably provided by the catalyst or absorber or the catalyst or absorber support.

The NO<sub>x</sub> absorber/trap comprises a compound including an alkali metal, an alkaline earth, rare earth metal or transition metal or a mixed oxide capable of forming nitrates and/or nitrites of adequate stability in non-reducing conditions and of evolving nitrogen oxides and/or nitrogen in reducing conditions, an oxidation catalyst, preferably Pt, and a reduction catalyst, preferably rhodium (Rh). Composite oxides of e.g. alkaline earth metal and copper can also be used, such as (adopting periodic table letter codes) Ba-Cu-O or MnO<sub>2</sub>-BaCuO<sub>2</sub>, possibly with added CeO<sub>2</sub>, or Y-Ba-Cu-O and Y-Sr-Co-O. The NO<sub>x</sub> reduction catalyst will generally include one or more PGM, but especially Pt, Pt/Rh, Pd/Rh or Pt/Pd/Rh. The SCR catalyst can be a copper-based material, Pt, a mixed oxide of vanadia (V<sub>2</sub>O<sub>5</sub>) and titania (TiO<sub>2</sub>) or a zeolite or mixtures of two or more thereof and is preferably V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub>. Reference can be made to our WO 99/55446 and WO 99/39809 for further information. The SO<sub>x</sub> absorber can include an alkaline earth metal oxide or alkali metal oxide or mixtures of any two or more thereof. Reference can be made to our EP-A-0814242 for further details.

In an exhaust system including an embodiment of the present invention including a NO<sub>x</sub> reduction catalyst or an SCR catalyst, the system can include means to inject reductant and/or NO<sub>x</sub>-specific reactant continuously or intermittently upstream of these catalysts. The oxidation catalyst of the invention can be in two parts, optimised respectively for oxidation of HC and CO and for conversion of NO to NO<sub>2</sub>. In the embodiment including both the NO<sub>x</sub> absorber and reduction catalyst, they can be in

distinct regions of the filter or associated, for example co-precipitated or co-impregnated or present as sandwiched layers or as relatively fine (e.g. 1-500  $\mu\text{m}$ ) particles or overlaid in different washcoats.

5            Preferably, the or each catalyst or absorber is supported on a high-surface oxide support, preferably alumina ( $\text{Al}_2\text{O}_3$ ),  $\text{TiO}_2$  or zirconia ( $\text{ZrO}_2$ ), but the or each catalyst or absorber can be supported directly by the filter i.e. without additional high-surface oxide support.

10           Desirably, the catalyst(s) and, where present, absorber(s), whether supported on a high surface area oxide or directly by the filter, increases the local pressure-drop of the wall-flow filter by a factor of at least 2, and preferably up to 10. In one embodiment, the filter zone itself can be catalysed. A suitable catalyst is an oxidation catalyst to assist in combusting the soot, but more preferably the catalyst includes a base metal such as  
15           magnesium oxide ( $\text{MgO}$ ) and most preferably the catalyst is a combination of lanthanum (La), caesium (Cs) and vanadium pentoxide ( $\text{V}_2\text{O}_5$ ). Where the base metal is  $\text{MgO}$ , a preferred catalyst is Pt on  $\text{MgO}$ . If the surfaces of the pores of the filter zone are to carry a catalyst, the pore diameter may be in the upper fifth of the above mentioned range or even higher, but such coating should be thin enough to avoid the need for large pores that  
20           would weaken the filter structurally.

             "Alkali metal" as defined herein includes potassium (K), sodium (Na), lithium (Li), rubidium (Rb) or Cs; "alkaline earth metal" includes barium (Ba), calcium (Ca), strontium (Sr) or magnesium (Mg); and "rare earth metal" includes cerium (Ce), La or  
25           yttrium (Y) or other lanthanides.

             The filter according to the invention can be packaged in any convenient way. Packaging materials commonly used in the art include a ceramic or steel wire mesh for wrapping and insulating the filter core; end plugs to prevent exhaust gas leaks through  
30           the wire mesh or to protect the mat; and steel for the shell or can. A suitable header can be used to provide the transition between the inlet and outlet pipes and the filter cross-section. Ports for the injection of additives or the introduction of sensor devices for on-board diagnostics can also be provided, where necessary.

The filter of the present invention can be made by methods known in the art, as exemplified by way of illustration only herebelow. In this aspect, the invention provides a method of making a filter according to the invention by stage-wise dipping in solutions and/or dispersions of precursors of the catalyst or absorber. In preferred features of this method, the method includes the steps of coating a wall of a channel of a wall-flow monolith with at least one material effective to decrease locally the gas permeability of the wall; and then applying to the coated wall at least one catalyst or absorber and optionally calcining the coated monolith.

However, we prefer to use the apparatus and method described in our WO 99/47260. To this end according to a further aspect, the invention provides a method of making a filter according to the invention comprising, in either order, the steps of: (i) locating a containment means on top of a wall-flow monolith having a plurality of channels in honeycomb arrangement, wherein at least some of the channels are plugged at an upstream end and at least some of the channels not plugged at the upstream end are plugged at a downstream end; and (ii) dosing a pre-determined quantity of a liquid being a washcoat slurry or a solution of a catalyst or catalyst precursor, or a mixture of the two, into the containment means; and then (iii) by applying pressure or a vacuum, drawing said liquid component into at least a portion of the open wall-flow monolith channels, and retaining substantially all of the quantity within the channels.

In an alternative embodiment, the above method is applied to an unplugged monolith and the channels are plugged after the coatings have been applied. If one end of a channel is to be plugged, the method includes the step of removing coating applied to that end prior to plugging. Alternatively, the method includes the step of coating only the ends of channels which are predetermined to remain unplugged, i.e. the coating is not applied to an end of a channel which is to be plugged.

In a preferred feature, the method according to the invention comprises the step of applying a resist to a region where application of a washcoat or a solution or suspension of a catalyst or catalyst precursor or mixture thereof is to be delayed. The resist can be a wax or stearic acid, for example.



exhaust system having a filter according to the invention. Preferably, the combustion engine is a diesel engine.

In another aspect, the invention provides a vehicle fitted with a combustion engine, preferably a diesel engine, including an exhaust system having a filter according to the invention.

According to a further aspect of the invention there is provided the use of a filter according to the invention for treating exhaust gases from a combustion engine, preferably a diesel engine.

In a further aspect, the invention provides a process for removing by combustion soot deposited on a filter disposed in an exhaust system of a combustion engine wherein exhaust gas containing NO is initially passed without filtering over an oxidation catalyst to convert NO in the exhaust gas to NO<sub>2</sub> prior to filtering to remove soot and wherein the exhaust gas containing NO<sub>2</sub> is then used to combust the soot trapped on the filter, the amount of NO converted to NO<sub>2</sub> being sufficient to enable combustion of soot trapped on the filter to proceed at a temperature less than 400°C, characterised in that the filter is a wall-flow filter, which filter comprises: a plurality of channels in honeycomb arrangement, wherein at least some of the channels are plugged at an upstream end and at least some of the channels not plugged at the upstream end are plugged at a downstream end; the oxidation catalyst is on a substantially gas impermeable zone at an upstream end of the channels plugged at the downstream end; and a gas permeable filter zone downstream of the oxidation catalyst for trapping soot.

In order that the invention may be more fully understood, reference will be made to the accompanying drawing which shows an elevated cross-sectional view of one embodiment of a filter according to the present invention.

Figure 1 shows three adjacent channels 4, 6, 8 of a cordierite honeycomb filter 10, having 200 cpsi (31 cm<sup>-2</sup>) and, before use, pores of approximately 10 µm in diameter. Channel 6 is plugged at 12 at the upstream end of the filter 10 and the other two channels 4, 8 are each plugged at 14 at the downstream end of the filter 10. Thus, gas entering

two channels 4,8 are each plugged at 14 at the downstream end of the filter 10. Thus, gas entering channel 6 at the upstream end must pass through the walls of the channel 6 to reach the downstream end of the filter 10. Over a region or zone extending downstream of the opening to channel 6, the walls carry coating 16 comprising an  $\text{Al}_2\text{O}_3$  washcoat support and a metallic Pt oxidation catalyst. Coating 16 obstructs the pores of the filter walls. Over a region or zone extending upstream from the outlet to filter 10, channels 4 and 8 carry coatings 18, 20 comprising a  $\text{NO}_x$  absorber composition including barium oxide ( $\text{BaO}$ ) and a  $\text{NO}_x$  reduction catalyst composition comprising Pt/Rh. In order to make the coatings 18, 20, the zone to be coated with coating 20 is first covered with a resist, such as wax or stearic acid, during application of coating 18. In this embodiment the regions of the cordierite filter 10 including coatings 16 and 18 are rendered gas impermeable by the presence of the coating. Between coatings 16 and 18, the walls of the channels 4, 6, 8 remain gas permeable and provide a filter zone 22.

Diesel exhaust gas entering the reactor undergoes oxidation of HC, CO and NO in presence of coating 16. Soot in the gas is collected on the walls of channels 4, 6, 8 at filter zone 22 and is combusted by  $\text{NO}_2$  derived from the oxidation of NO. The gas, containing soot combustion products, passes through the wall of the filter and contacts the  $\text{NO}_x$  trap coating 18, which absorbs  $\text{NO}_2$ . When sufficient  $\text{NO}_2$  is stored (as the nitrate, for example), which can be ascertained by the on-board diagnostics of the vehicle, coating 18 can be regenerated with a rich pulse of gaseous exhaust i.e. gas including excess reductant such as HC. The rich/lean cycling can be controlled using the vehicle's engine management system. The resulting  $\text{NO}_x$ -rich gas contacts coating 20 including the  $\text{NO}_x$  reduction catalyst, which effects oxidation of HC and CO and reduction of  $\text{NO}_x$  to  $\text{N}_2$ . Alternatively, where coating 20 is a SCR catalyst,  $\text{NO}_x$ -specific reactant such as ammonia can be injected at an upstream end of the filter at a rate and temperature permitting unreacted ammonia to slip oxidation catalyst 16 and contact absorber 18, which it regenerates, and catalyst 20, over which it reduces  $\text{NO}_x$  to  $\text{N}_2$ .

In order that one method of manufacture of the filter according to the invention may be more fully understood, the following Example is provided by way of illustration only.

The substrate is a filter grade cordierite honeycomb monolith of square cross-section channels 30 mm in diameter and 150 mm long and having a mean pore diameter 10  $\mu\text{m}$  in which half of the passages both ends of the monolith are plugged so that each channel of the monolith is plugged at one or other end thereof, and at the opposite end to the laterally and vertically adjacent channels.

One end of the monolith is labelled 'inlet' and is dipped 25 mm deep into an aqueous dispersion of hydrated  $\text{Al}_2\text{O}_3$ , then withdrawn, dried at  $100^\circ\text{C}$  and allowed to cool. The inlet end is then dipped to the same depth in an aqueous solution of 2% w/w platinum chloride. The monolith is dried as before.

The unlabelled end of the monolith is prepared by firstly dipping it to a depth of 25 mm in turn in an aqueous solution of sodium stearate and then drying the resulting monolith at  $100^\circ\text{C}$ . The resulting monolith is then dipped in aqueous hydrochloric acid and then water (two changes), to rinse off solubles. This procedure produces an insoluble stearic acid layer as a resist, which excludes any materials applied in neutral or acidic solution. The resist-coated monolith is then dipped to a depth of 50 mm, into an aqueous solution of barium acetate and platinum chloride, and then dried. This dip applies these materials to an area upstream of the resist-coated area. Then the coated monolith is dipped in 5% w/w aqueous sodium hydroxide to a depth of 25 mm to dissolve the stearic acid resist. This step is repeated twice and is followed by two rinses with water. The coated monolith is then dried. The resulting monolith is then dipped to a depth of 25 mm in the  $\text{Al}_2\text{O}_3$  dispersion used at the inlet end, and described above. The coated monolith is then dried. Finally, to a depth of 25 mm in Pt/Rh solution. The coated monolith is then dried.

The resulting monolith is then calcined at  $500^\circ\text{C}$  for 1 hr to convert the metal salts to oxides or metals and to develop the surface area of the  $\text{Al}_2\text{O}_3$  to provide a filter according to the invention.

**CLAIMS:**

1. A wall-flow filter (10) for an exhaust system of a combustion engine, which filter comprises: a plurality of channels (4,6,8) in honeycomb arrangement, wherein at least  
5 some of the channels (6) are plugged (12) at an upstream end and at least some of the channels (4,8) not plugged at the upstream end are plugged (14) at a downstream end; an oxidation catalyst (16) on a substantially gas impermeable zone at an upstream end of the channels (4,8) plugged at the downstream end; and a gas permeable filter zone (22) downstream of the oxidation catalyst for trapping soot, characterised in that in an exhaust  
10 system the oxidation catalyst is capable of generating sufficient NO<sub>2</sub> from NO to combust the trapped soot continuously at a temperature less than 400°C.
2. A filter according to claim 1, wherein the filter is made of a ceramic material, preferably cordierite, alumina, mullite, silicon carbide, zirconia or  
15 sodium/zirconia/phosphate.
3. A filter according to claim 1 or 2, wherein the channels of the honeycomb are square, circular, rectangular, hexagonal or triangular in cross section.
- 20 4. A filter according to claim 1, 2 or 3, wherein, the arrangement of plugged upstream and downstream channels is such that each channel is plugged at one or other end thereof, and at the opposite end to the laterally and vertically adjacent channels.
5. A filter according to claim 1, 2 or 3, wherein at least some of the channels are  
25 unplugged to provide a flow-through by-pass to the filter channels. .
6. A filter according to any of claims 1 to 5, wherein the oxidation catalyst includes a platinum group metal (PGM), preferably Pt and/or Pd.
- 30 7. A filter according to any of claims 1 to 6, wherein the filter zone includes a catalyst which facilitates the soot combustion.
8. A filter according to claim 7, wherein the combustion catalyst comprises a base

metal.

9. A filter according to claim 8, wherein the combustion catalyst comprises a combination of lanthanum, caesium and vanadium pentoxide or is Pt on MgO.

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10. A filter according to any preceding claim, further comprising a NOx absorber (18) on a substantially gas impermeable zone on the channels (6) plugged at the upstream end.

10 11. A filter according to claim 10, wherein the NOx absorber includes an alkali metal, an alkaline earth metal or rare earth metal or mixtures of any two or more thereof.

12. A filter according to claim 10 or 11, wherein the NOx absorber includes a mixed oxide.

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13. A filter according to claim 10, 11 or 12, further comprising a NOx reduction catalyst or a Selective Catalytic Reduction (SCR) catalyst (20) on a substantially gas impermeable zone on the channels downstream of the NOx absorber (18).

20 14. A filter according to claim 13, wherein the SCR catalyst includes copper-based materials, Pt, a mixed oxide of vanadium and titania or a zeolite or mixtures of two or more thereof and is preferably  $V_2O_5/WO_3/TiO_2$ .

25 15. A filter according to claim 14, wherein the NOx reduction catalyst comprises one or more PGM, preferably Pt, Pt/Rh, Pd/Rh or Pt/Pd/Rh.

16. A filter according to any preceding claim, further comprising a SOx absorber on a substantially gas impermeable zone on the channels upstream of the oxidation catalyst.

30 17. A filter according to claim 16, wherein the SOx absorber includes an alkaline earth metal oxide or alkali metal oxide or mixtures of any two or more thereof.

18. A filter according to claim 11 or 17, wherein the alkali metal is potassium,

sodium, lithium, rubidium or caesium or a mixture of any two or more thereof, the alkaline earth metal is barium, calcium, strontium or magnesium or a mixture of any two or more thereof or the rare earth metal is cerium, lanthanum or yttrium or other lanthanide or a mixture of any two or more thereof.

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19. A filter according to any preceding claim, wherein the or each catalyst or absorber is supported on a high-surface oxide support, preferably alumina, titania or zirconia.

20. A filter according to any preceding claim, wherein the catalyst or absorber or a support supporting the catalyst or absorber renders the zone including the catalyst or  
10 absorber substantially gas impermeable.

21. A filter according to any preceding claim, wherein the presence of each catalyst or absorber on a wall-flow filter increases the local pressure drop of the wall-flow filter by a factor of at least 2, preferably at least 10.

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22. A combustion engine including an exhaust system having a filter according to any preceding claim.

23. A diesel engine according to claim 22.

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24. A vehicle fitted with a combustion engine according to claim 22 or 23.

25. A process for removing by combustion soot deposited on a filter disposed in an exhaust system of a combustion engine wherein exhaust gas containing NO is initially  
25 passed without filtering over an oxidation catalyst to convert NO in the exhaust gas to NO<sub>2</sub> prior to filtering to remove soot and wherein the exhaust gas containing NO<sub>2</sub> is then used to combust the soot trapped on the filter, the amount of NO converted to NO<sub>2</sub> being sufficient to enable combustion of soot trapped on the filter to proceed at a temperature less than 400°C, characterised in that the filter is a wall-flow filter (10), which filter  
30 comprises: a plurality of channels (4,6,8) in honeycomb arrangement, wherein at least some of the channels (6) are plugged (12) at an upstream end and at least some of the channels (4,8) not plugged at the upstream end are plugged (14) at a downstream end; the oxidation catalyst (16) is on a substantially gas impermeable zone at an upstream end of

the channels (4,8) plugged at the downstream end; and a gas permeable filter zone (22) downstream of the oxidation catalyst for trapping soot.

26. The use of a filter according to any of claims 1 to 21 for treating exhaust gases from a combustion engine, preferably a diesel engine.

27. A method of making a filter according to any preceding claim, which method comprising, in either order, the steps of: (i) locating a containment means on top of a wall-flow monolith having a plurality of channels in honeycomb arrangement, wherein at least some of the channels are plugged at an upstream end and at least some of the channels not plugged at the upstream end are plugged at a downstream end; and (ii) dosing a pre-determined quantity of a liquid being a washcoat slurry or a solution of a catalyst or catalyst precursor, or a mixture of the two, into the containment means; and then (iii) by applying pressure or a vacuum, drawing said liquid component into at least a portion of the open wall-flow monolith channels, and retaining substantially all of the quantity within the channels.

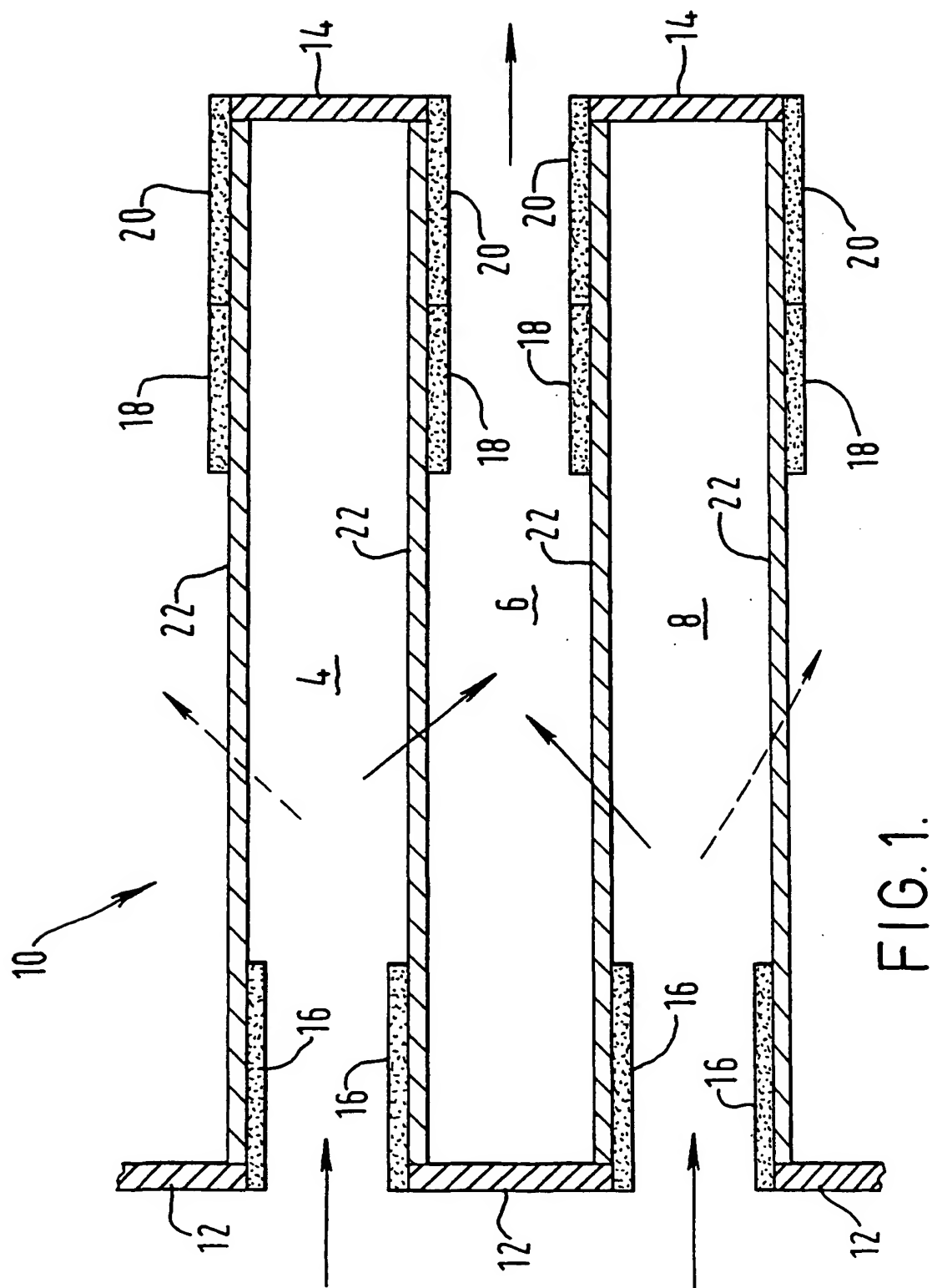
28. A method of making a filter according to any of claims 1 to 21, by stage-wise dipping in solutions and/or dispersions of precursors of the catalyst or absorber.

29. A method according to claim 27 which comprises: coating a wall of a channel of a wall flow monolith with at least one material effective to decrease locally the gas permeability of the wall; and then applying to the coated wall at least one catalyst or absorber.

30. A method according to any of claims 25 to 29, which comprises applying a resist to a region where application of a washcoat or a solution or mixture thereof is to be delayed.

31. A method according to claim 27, 28 or 29 which comprises calcining the coated monolith.

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# INTERNATIONAL SEARCH REPORT

Intern 1al Application No

PCT/GB 00/03064

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/56 B01D53/94 B01J35/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 00 29726 A (ENGELHARD CORP) 25 May 2000 (2000-05-25) samples 4 and 6 page 26; table I	1-8, 22-31
X	EP 0 834 343 A (TOYODA CHUO KENKYUSHO KK) 8 April 1998 (1998-04-08) Embodiment 3	1-8, 22-31
X	US 5 089 237 A (LANGER HANS-JOACHIM ET AL) 18 February 1992 (1992-02-18) column 3 and Figure in combination with content of EP-A-277012 cited in the application	1-7, 22-26
Y	the whole document	1-9, 22-31
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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Date of the actual completion of the international search

28 November 2000

Date of mailing of the international search report

19/12/2000

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## INTERNATIONAL SEARCH REPORT

Internat'l Application No

PCT/GB 00/03064

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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L	EP 0 277 012 A (NGK INSULATORS LTD) 3 August 1988 (1988-08-03) cited in US-A-5089237; describes that the filter used in US-A-5089237 has channels which are plugged upstream page 3, line 18 -page 3, line 22 ---	
X	US 4 515 758 A (DOMESLE RAINER ET AL) 7 May 1985 (1985-05-07) example 4 ---	1-8
Y	EP 0 341 832 A (JOHNSON MATTHEY INC) 15 November 1989 (1989-11-15) cited in the application claims; example 4 ---	1-9, 22-31
A	EP 0 758 713 A (TOYOTA MOTOR CO LTD) 19 February 1997 (1997-02-19) cited in the application ---	
A	WO 99 39809 A (GOERSMANN CLAUS FRIEDRICH ;JOHNSON MATTHEY PLC (GB); CHANDLER GUY) 12 August 1999 (1999-08-12) cited in the application -----	

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Information on patent family members

International Application No.

PCT/GB 00/03064

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